

Figure 1. The effect of the concentration of the *Agaricus bisporus* spores on the growth of *Agaricus bisporus* on the substrate. The concentration of the spores was 10⁴ spores/ml (a), 10⁵ spores/ml (b), 10⁶ spores/ml (c), 10⁷ spores/ml (d), 10⁸ spores/ml (e), 10⁹ spores/ml (f), 10¹⁰ spores/ml (g), 10¹¹ spores/ml (h), 10¹² spores/ml (i), 10¹³ spores/ml (j), 10¹⁴ spores/ml (k), 10¹⁵ spores/ml (l), 10¹⁶ spores/ml (m), 10¹⁷ spores/ml (n), 10¹⁸ spores/ml (o), 10¹⁹ spores/ml (p), 10²⁰ spores/ml (q), 10²¹ spores/ml (r), 10²² spores/ml (s), 10²³ spores/ml (t), 10²⁴ spores/ml (u), 10²⁵ spores/ml (v), 10²⁶ spores/ml (w), 10²⁷ spores/ml (x), 10²⁸ spores/ml (y), 10²⁹ spores/ml (z), 10³⁰ spores/ml (aa), 10³¹ spores/ml (ab), 10³² spores/ml (ac), 10³³ spores/ml (ad), 10³⁴ spores/ml (ae), 10³⁵ spores/ml (af), 10³⁶ spores/ml (ag), 10³⁷ spores/ml (ah), 10³⁸ spores/ml (ai), 10³⁹ spores/ml (aj), 10⁴⁰ spores/ml (ak), 10⁴¹ spores/ml (al), 10⁴² spores/ml (am), 10⁴³ spores/ml (an), 10⁴⁴ spores/ml (ao), 10⁴⁵ spores/ml (ap), 10⁴⁶ spores/ml (aq), 10⁴⁷ spores/ml (ar), 10⁴⁸ spores/ml (as), 10⁴⁹ spores/ml (at), 10⁵⁰ spores/ml (au), 10⁵¹ spores/ml (av), 10⁵² spores/ml (aw), 10⁵³ spores/ml (ax), 10⁵⁴ spores/ml (ay), 10⁵⁵ spores/ml (az), 10⁵⁶ spores/ml (ba), 10⁵⁷ spores/ml (bb), 10⁵⁸ spores/ml (bc), 10⁵⁹ spores/ml (bd), 10⁶⁰ spores/ml (be), 10⁶¹ spores/ml (bf), 10⁶² spores/ml (bg), 10⁶³ spores/ml (bh), 10⁶⁴ spores/ml (bi), 10⁶⁵ spores/ml (bj), 10⁶⁶ spores/ml (bk), 10⁶⁷ spores/ml (bl), 10⁶⁸ spores/ml (bm), 10⁶⁹ spores/ml (bn), 10⁷⁰ spores/ml (bo), 10⁷¹ spores/ml (bp), 10⁷² spores/ml (bq), 10⁷³ spores/ml (br), 10⁷⁴ spores/ml (bs), 10⁷⁵ spores/ml (bt), 10⁷⁶ spores/ml (bu), 10⁷⁷ spores/ml (bv), 10⁷⁸ spores/ml (bw), 10⁷⁹ spores/ml (bx), 10⁸⁰ spores/ml (by), 10⁸¹ spores/ml (bz), 10⁸² spores/ml (ca), 10⁸³ spores/ml (cb), 10⁸⁴ spores/ml (cc), 10⁸⁵ spores/ml (cd), 10⁸⁶ spores/ml (ce), 10⁸⁷ spores/ml (cf), 10⁸⁸ spores/ml (cg), 10⁸⁹ spores/ml (ch), 10⁹⁰ spores/ml (ci), 10⁹¹ spores/ml (cj), 10⁹² spores/ml (ck), 10⁹³ spores/ml (cl), 10⁹⁴ spores/ml (cm), 10⁹⁵ spores/ml (cn), 10⁹⁶ spores/ml (co), 10⁹⁷ spores/ml (cp), 10⁹⁸ spores/ml (cq), 10⁹⁹ spores/ml (cr), 10¹⁰⁰ spores/ml (cs), 10¹⁰¹ spores/ml (ct), 10¹⁰² spores/ml (cu), 10¹⁰³ spores/ml (cv), 10¹⁰⁴ spores/ml (cw), 10¹⁰⁵ spores/ml (cx), 10¹⁰⁶ spores/ml (cy), 10¹⁰⁷ spores/ml (cz), 10¹⁰⁸ spores/ml (da), 10¹⁰⁹ spores/ml (db), 10¹¹⁰ spores/ml (dc), 10¹¹¹ spores/ml (dd), 10¹¹² spores/ml (de), 10¹¹³ spores/ml (df), 10¹¹⁴ spores/ml (dg), 10¹¹⁵ spores/ml (dh), 10¹¹⁶ spores/ml (di), 10¹¹⁷ spores/ml (dj), 10¹¹⁸ spores/ml (dk), 10¹¹⁹ spores/ml (dl), 10¹²⁰ spores/ml (dm), 10¹²¹ spores/ml (dn), 10¹²² spores/ml (do), 10¹²³ spores/ml (dp), 10¹²⁴ spores/ml (dq), 10¹²⁵ spores/ml (dr), 10¹²⁶ spores/ml (ds), 10¹²⁷ spores/ml (dt), 10¹²⁸ spores/ml (du), 10¹²⁹ spores/ml (dv), 10¹³⁰ spores/ml (dw), 10¹³¹ spores/ml (dx), 10¹³² spores/ml (dy), 10¹³³ spores/ml (dz), 10¹³⁴ spores/ml (ea), 10¹³⁵ spores/ml (eb), 10¹³⁶ spores/ml (ec), 10¹³⁷ spores/ml (ed), 10¹³⁸ spores/ml (ee), 10¹³⁹ spores/ml (ef), 10¹⁴⁰ spores/ml (eg), 10¹⁴¹ spores/ml (eh), 10¹⁴² spores/ml (ei), 10¹⁴³ spores/ml (ej), 10¹⁴⁴ spores/ml (ek), 10¹⁴⁵ spores/ml (el), 10¹⁴⁶ spores/ml (em), 10¹⁴⁷ spores/ml (en), 10¹⁴⁸ spores/ml (eo), 10¹⁴⁹ spores/ml (ep), 10¹⁵⁰ spores/ml (eq), 10¹⁵¹ spores/ml (er), 10¹⁵² spores/ml (es), 10¹⁵³ spores/ml (et), 10¹⁵⁴ spores/ml (eu), 10¹⁵⁵ spores/ml (ev), 10¹⁵⁶ spores/ml (ew), 10¹⁵⁷ spores/ml (ex), 10¹⁵⁸ spores/ml (ey), 10¹⁵⁹ spores/ml (ez), 10¹⁶⁰ spores/ml (fa), 10¹⁶¹ spores/ml (fb), 10¹⁶² spores/ml (fc), 10¹⁶³ spores/ml (fd), 10¹⁶⁴ spores/ml (fe), 10¹⁶⁵ spores/ml (ff), 10¹⁶⁶ spores/ml (fg), 10¹⁶⁷ spores/ml (fh), 10¹⁶⁸ spores/ml (fi), 10¹⁶⁹ spores/ml (fj), 10¹⁷⁰ spores/ml (fk), 10¹⁷¹ spores/ml (fl), 10¹⁷² spores/ml (fm), 10¹⁷³ spores/ml (fn), 10¹⁷⁴ spores/ml (fo), 10¹⁷⁵ spores/ml (fp), 10¹⁷⁶ spores/ml (fq), 10¹⁷⁷ spores/ml (fr), 10¹⁷⁸ spores/ml (fs), 10¹⁷⁹ spores/ml (ft), 10¹⁸⁰ spores/ml (fu), 10¹⁸¹ spores/ml (fv), 10¹⁸² spores/ml (fw), 10¹⁸³ spores/ml (fx), 10¹⁸⁴ spores/ml (fy), 10¹⁸⁵ spores/ml (fz), 10¹⁸⁶ spores/ml (ga), 10¹⁸⁷ spores/ml (gb), 10¹⁸⁸ spores/ml (gc), 10¹⁸⁹ spores/ml (gd), 10¹⁹⁰ spores/ml (ge), 10¹⁹¹ spores/ml (gf), 10¹⁹² spores/ml (gg), 10¹⁹³ spores/ml (gh), 10¹⁹⁴ spores/ml (gi), 10¹⁹⁵ spores/ml (gj), 10¹⁹⁶ spores/ml (gk), 10¹⁹⁷ spores/ml (gl), 10¹⁹⁸ spores/ml (gm), 10¹⁹⁹ spores/ml (gn), 10²⁰⁰ spores/ml (go), 10²⁰¹ spores/ml (gp), 10²⁰² spores/ml (gq), 10²⁰³ spores/ml (gr), 10²⁰⁴ spores/ml (gs), 10²⁰⁵ spores/ml (gt), 10²⁰⁶ spores/ml (gu), 10²⁰⁷ spores/ml (gv), 10²⁰⁸ spores/ml (gw), 10²⁰⁹ spores/ml (gx), 10²¹⁰ spores/ml (gy), 10²¹¹ spores/ml (gz), 10²¹² spores/ml (ha), 10²¹³ spores/ml (hb), 10²¹⁴ spores/ml (hc), 10²¹⁵ spores/ml (hd), 10²¹⁶ spores/ml (he), 10²¹⁷ spores/ml (hf), 10²¹⁸ spores/ml (hg), 10²¹⁹ spores/ml (hh), 10²²⁰ spores/ml (hi), 10²²¹ spores/ml (hj), 10²²² spores/ml (hk), 10²²³ spores/ml (hl), 10²²⁴ spores/ml (hm), 10²²⁵ spores/ml (hn), 10²²⁶ spores/ml (ho), 10²²⁷ spores/ml (hp), 10²²⁸ spores/ml (hq), 10²²⁹ spores/ml (hr), 10²³⁰ spores/ml (hs), 10²³¹ spores/ml (ht), 10²³² spores/ml (hu), 10²³³ spores/ml (hv

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METHOD OF FORMING REFRACTORY METAL CONTACT IN AN OPENING, AND RESULTING STRUCTURE

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FIELD OF THE INVENTION

This invention relates to a method of forming a refractory metal contact over a silicon substrate in a solid state structure, and to related structures. More particularly, the invention relates to a method employing a sacrificial silicon layer that serves as a nucleation layer for subsequent deposition of a refractory material to form a contact.

BACKGROUND OF THE INVENTION

Conductive metal contacts are frequently found in semiconductor devices, and typically are formed by deposition of a refractory material, such as tungsten or the like, confined by a silicon oxide layer previously deposited over a conducting substrate containing, for example, a silicide. Steps in the conventional method of forming such contacts, and the nature of a problem that sometimes arises, are best understood with reference to Figures 1, 2, 3 and 4(A)-(B) hereof.

Figure 1 is a cross-sectional view of a relevant portion of the underlying structure, wherein an underlying silicide layer 100 serves as a substrate 4 with an oxide layer 102 formed thereon. The location, shape and size of the desired conductor is determined by a through opening 104 formed in the oxide layer 102, with exposed surface 106 of the silicide serving as a bottom 106 of the opening 104. As best seen in Figure 2, a thin metallic layer 200 is then deposited at the bottom of aperture 104 to serve as a contact liner. Then, per Figure 3, a thin nucleation layer 300 of a refractory material such as

10 tungsten is formed in the presence of silane gas to cover oxide layer 102, the sides 108 of
aperture 104, per liner 200. This is followed, per Figure 4(A), by the deposition of a layer
400 containing the desired refractory material in an amount sufficient to totally cover and
fill up the inside of aperture 104 and to extend over the upper surface of oxide layer 102.
5 Note that the nucleation layer 300 becomes, in effect, absorbed within the refractory layer
400.

10 Unfortunately, when a refractory material such as tungsten is deposited from
decomposition of WF_6 through the use of either physical vapor deposition (PVD) or
chemical vapor deposition (CVD), particularly during a chemical vapor deposition step,
some of the fluorine released from decomposition of WF_6 combines with silicon in the
silicide layer 100 and a propensity to form an undesirable region 402, as is probably best
seen in the enlarged view in Figure 4(B).

15 An example of a prior patent which appears to address a similar problem is US
Patent 5,804, 499, to Dehm et al., titled "Prevention of Abnormal WSi_x Oxidation by In-
Situ Amorphous Silicon Deposition", which suggests a process in which amorphous
silicon is deposited in a thin layer on top of tungsten silicide to prevent abnormal WSi_x
oxidation during subsequent process steps. The layer of amorphous silicon as mentioned
in this patent is bounded by a spacer also made of amorphous silicon. The reference does
not teach the provision of a continuous layer of silicon to address the problem at issue.

20 The present invention seeks to address this particular problem in a simple and
efficient manner.

SUMMARY OF THE INVENTION

25 This invention provides a method by which a refractory material may be
deposited in and over an opening in a non-conducting layer over a conducting layer,
employing a known PVD or CVD step, without damage to the underlying conducting
layer.

30 The present invention also provides a structure which includes a refractory
material contact formed over an opening in a non-conductive layer deposited over a
conductive metal silicide layer.

Accordingly, in a first aspect of this invention, there is provided a method of filling an opening in an oxide layer, over a liner layer formed on a silicide layer underlying both the oxide layer and the liner layer, which includes the step of forming a continuous first layer of silicon on the oxide layer, a wall of the opening and the liner layer and, thereafter, forming a second layer of a refractory material on the first layer so as to cover the same and to also substantially fill the opening.

In another aspect of this invention, there is provided a multi-layer structure which includes a silicide layer having a first surface; an oxide layer formed on the first surface and having a second surface with a through opening defined in the oxide layer from the second surface to the first surface; a liner layer formed on the first surface at a bottom of the opening, a continuous silicon layer formed to extend over the second surface, the opening surface and the liner layer; and a refractory material layer formed on the silicon layer so as to substantially fill the opening.

These and other aspects, objectives and advantages of the present invention will become clearer from an understanding of the following detailed description with reference to the appended figures.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1, 2, 3 and 4(A)-(B) all relate to the prior art.

Figure 1 is a cross-sectional view showing a metal silicide layer over which is formed a non-conducting oxide layer with a through aperture defined therein.

Figure 2 is a cross-sectional view showing the structure per Figure 1, with a metallic liner layer formed at a bottom surface of the aperture.

Figure 3 is a cross-sectional view at a stage following Figure 2, showing the deposition of a nucleation layer 300 of tungsten over the oxide layer, the sides of the opening formed therein, and the liner at the bottom of the opening.

Figure 4(A) is a cross-sectional view at a later stage in the known process, wherein a deposit of a refractory material covers the oxide layer and fills the opening above the liner, and also indicates the presence of an undesirable region that may

sometimes be formed during deposition of the refractory material due to interaction with the underlying silicide.

Figure 4(B) is an enlarged view of a relevant portion of Figure 4(A), to show more clearly the undesired contamination of the underlying silicide layer at the bottom of the opening that is otherwise filled with refractory material.

Figure 5, per the method according to the present invention, is a cross-sectional view of the structure per Figure 2 with the deposit of a continuous silicon layer over the oxide layer, the sides of the opening formed therein, and the underlying liner at the bottom of the opening.

Figure 6 is a cross-sectional view after deposition of a refractory material over the continuous silicon layer shown in Figure 5.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

As indicated above, the present invention is aimed at providing a method that ensures against contamination of an underlying silicide substrate by any constituent of a refractory conducting layer during its deposition into the desired structure.

Referring to the structure illustrated in cross-sectional view in Figure 2, note that a silicide layer 100, of the order of 300-800 Å in thickness and deposited on a silicon substrate 150, typically serves as a substrate for an oxide layer 102 deposited thereon with a through opening 104 defined therein, with a liner layer 200 deposited at the bottom 106 of opening 104 in known manner. Liner layer 200 may comprise at least one of titanium, titanium nitride, tungsten, and an alloy of titanium and tungsten, and may incidentally be deposited on the oxide layer 102. The preferred method according to this invention includes these steps of the prior art.

In the prior art, as best understood with reference to Figure 3, a layer 300 of tungsten (W) deposited from WF_6 decomposition in the presence of silane was then formed as a nucleation layer.

According to the present invention, a continuous layer 500 of amorphous or polycrystalline silicon is deposited to a controlled thickness preferably by either physical

vapor depositions (PVD) or by chemical vapor deposition (CVD), to extend over the oxide layer 102 and the upper surface of liner layer 200. This is best understood with reference to Figure 5.

5 The continuous silicon layer 500 is intended to be a sacrificial layer, i.e., it is anticipated that it may chemically interact and combine with any fluorine (F) that becomes available when, for example, WF_6 is decomposed to generate a tungsten contact layer 400. In other words, it is intended in the present invention that some of this silicon be consumed in preference to any silicon from the underlying silicide layer 100. The deposited silicon layer 500 must be in the form of a continuous amorphous or
10 polycrystalline silicon layer. The deposited polysilicon may be obtained by decomposition of a silane such as silane, disilane or trisilane. However, silanes containing ions such as dichlorosilane may advantageously be used and are preferred for this purpose.

15 The resulting structure is best understood with reference to Figure 6, in which the silicide substrate 100 supports oxide layer 102 and liner 200, and the continuous sacrificial amorphous or polycrystalline silicon layer 500 formed thereon serves as a base for the refractory layer 600 which extends over oxide layer 102 and substantially fills the opening 104. Note that a small imperfectly filled region 502 may exist in the refractory material 600 within the volume of the substantially filled opening 104 without any
20 deleterious effects on the resulting contact structure and its functionality.

The structure as illustrated in Figure 6 can then be subjected to conventional subsequent processing such as planarization of 600, 500 and 200.

As previously indicated, the present invention is intended to provide a satisfactory refractory layer while avoiding the known problems associated with the related prior art.
25 It is intended, further, that the "refractory material" may be a refractory metal, e.g., tungsten, titanium, tantalum or molybdenum employed directly as a "metal"; a refractory metal employed as a constituent of a "compound" thereof, e.g., titanium nitride, tantalum nitride, etc.; or even as a constituent of an "alloy" with another metal, e.g., titanium-tungsten. With any of these available options, the provision of a continuous silicon layer
30 as discussed above ensures against the known problem.

It is intended that the desired refractory material layer 600 be formed in known manner by either a PVD or CVD process step.

It is preferred that the continuous sacrificial silicon layer 500 be provided as an amorphous or polysilicon film of a thickness not greater than about 50 Å.

The application of the continuous sacrificial silicon layer 500 by either the PVD or the CVD process is preferably accomplished at a temperature in the range 500°-650°C, with 600°C being particularly preferred. It should be noted that when a PVD process is employed there may be little or no deposition of the silicon on sides 108, 108 of opening 104.

It should also be noted that the traditional way of providing a silicon deposition is to flow the silane gas in one process chamber over the underlying structure and, subsequent to depositing the desired silicon layer, to move the wafer supporting the desired structure into another process chamber where a WF_6 environment, for example, could be provided for the subsequent step of depositing tungsten thereon. An obvious problem in doing this is that the timing and conditions required to form the proper layer of silicon to protect the wafer from the chemically active WF_6 gas has a narrow process window and is subject to control problems.

The present invention, by utilizing the silicon layer as it does, i.e., as both a sacrificial layer and a nucleation layer, advantageously eliminates the need to do this. In other words, the wafer may be maintained in a single chamber and first be exposed to the silane or dichlorosilane to obtain the desired silicon layer under controlled conditions of time, temperature and flow rate, and this may be followed by passage of WF_6 gas over the same wafer in the same chamber under appropriate process conditions of controlled temperature, pressure and flow rate. The process is readily adaptable to either physical vapor deposition or chemical vapor deposition conducted in known manner. Any adaptation to employ any refractory metal, compound or alloy, may be made in known manner. It is considered that under all circumstances such as these, the sacrificial use of the continuous polysilicon film as taught in this invention ensures against deterioration of the underlying silicide layer.

